EFFECT OF DIFFERENT MESOSTRUCTURED MATERIAL BASED ON SILICA (TiO_2, SBA-15 AND CAB-O-SIL) AS COBALT SUPPORTS FOR FISCHER-TROPSCH SYNTHESIS

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ABSTRACT

The research was about the synthesis of active and selective for syngas processing via Fischer–Tropsch synthesis (FTS) producing clean and best fuel. A series of 20 wt. % cobalt catalysts be prepared by impregnation of a mesoporous molecular sieve based on silica as 75 wt. % of cobalt catalytic supporters (SBA-15, TiO_2 and Cab-O-Sil) with 5 wt. % Zn promoter for comparison purposes. All materials used characterizing by several analysis equipments which are SEM, TGA and FTIR. The characterization results achieve gave a great influence of mesoporous support porosity on the structure, reducibility of cobalt oxide species supported over the selected materials. Firstly, the experiment was started from the synthesis of SBA-15. TiO_2 and Cab-O-Sil are commercialized support. Then, the silica as cobalt supporters were synthesized by incipient wetness impregnation method of using mixture of Cobalt (II) Nitrate and Zinc Nitrate Hexahydrate solution. Next, the prepared catalysts were calcined at 350°C for 6 h by increasing the temperature at a controlled heating rate of 2°C/min. The characterization of catalysts and catalyst studies was performed. The result from experiment was SBA-15 supporter shown the better result compared to other samples as the microscopic size captured by SEM equipment prove that SBA-15 had smoothest and smallest of mesoporous surface size. The result from FTIR showed that the peak at around 3,440 cm^{-1} have the hydroxyl groups and about 1,630 cm^{-1} is due to the bending vibrations of O-H bonds that the percentage reflectance of O-H bonds which indicates the SBA-15 can effectively restrain the loss of surface hydroxyl groups during calcinations. The peak around 1000-1200 cm^{-1} can be assigned to the siloxane or Si-O-Si stretching bands; peak appears as a broad and strong peaking the sample. Lastly, TGA result showed that SBA-15 can help the catalyst samples restrained more water content in the evaporation process and had high thermal stability that can prolong life at high temperature and high pressure in the Fischer-Tropsch synthesis. The new silica as cobalt supporter will be developed to enhance the performance of the best and clean fuel production. This research hopefully can be carried out successful in order to get the new invention for production of catalyst that will produce the best and clean fuel and to get rid of exceed cost of production but in the same quality of expensive product.

ABSTRAK

Penyelidikan itu kira-kira sintesis aktif dan selektif untuk syngas pemprosesan melalui sintesis Fischer-Tropsch (FTS) menghasilkan bahan api bersih dan terbaik. Satu siri 20% berat. Pemangkin kobalt disediakan oleh penghamilan liang meso molekul berdasarkan silika sebagai 75% berat. Daripada penyokong sebagai pemangkin kobalt (SBA-15, TiO_2 dan Cab-O-Sil) dengan 5% berat. Penganjur Zn untuk tujuan perbandingan. Semua bahan yang digunakan mencirikan oleh beberapa peralatan analisis seperti SEM, TGA dan FTIR. Keputusan pencirian mencapai memberikan pengaruh yang besar sokongan keliangan pada struktur liang meso, pengurangan spesis oksida kobalt yang disokong ke atas bahan-bahan yang dipilih. Pertama, eksperimen bermula dari sintesis SBA-15 tetapi TiO_2 dan Cab-O-Sil adalah penyokong yang telah dikomersialkan. Kemudian, silika sebagai penyokong kobalt telah disintesis oleh keadah pembasahan menggunakan Kobalt (II) nitrat dan Zink nitrat Hexahydrat. Seterusnya, sample yang terhasil dioksidakan pada suhu 350°C selama 6 jam dengan kadar peningkatan sebanyak 2°C/min. Pencirian dan kajian pemangkin dilakukan. Keputusan dari eksperimen adalah SBA-15 penyokong menunjukkan hasil yang lebih baik berbanding dengan sampel lain seperti saiz mikroskopik yang ditangkap oleh peralatan SEM membuktikan bahawa SBA-15 permukaan liang meso paling rata dan saiz liang meso paling kecil. Dari keputusan FTIR menunjukkan bahawa puncak dalam lingkungan 3,440 cm-1 menpunyai kumpulan hidrosil dan pada 1,630 cm-1 disebabkan bengkokan getaran ikatan O-H yang menunjukan peratusan kereflekan ikatan O-H dalam SBA-15 menolong kehilangan permukaan kumpulan hidrosil ketika pengoksidaan. Puncak pada 1000-1200 cm-1 menentukan kumpulan siloxane or ikatan kembangan Si-O-Si; puncak yang tinggi kelihatan. Akhir sekali, hasil TGA menunjukkan bahawa SBA-15 boleh membantu sampel pemangkin menahan lebih kandungan air dalam proses penyejatan dan kestabilan haba yang tinggi yang boleh memanjangkan jangka hayat pada suhu tinggi dan tekanan tinggi dalam sintesis Fischer-Tropsch. Silika baru sebagai penyokong kobalt akan dimajukan untuk meningkatkan prestasi pengeluaran bahan api yang terbaik dan bersih. Kajian ini diharapkan dapat dijalankan berjaya untuk menghasilkan ciptaan baru bagi pengeluaran pemangkin yang akan menghasilkan bahan api yang terbaik dan bersih dan mengurangkan lebihan kos pengeluaran tetapi dalam kualiti yang sama produk mahal.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER ONE

INTRODUCTION

1.1. Background of Research

The invention of the original process was released by Franz Fischer and Hans Tropsch since they were working at the Kaiser Wilhelm Institute in the 1920s and there are many refinements and adjustments have been made. The term "Fischer-Tropsch" was applies now to a wide variety of similar processes or more commonly with the name of Fischer-Tropsch.

The Fischer–Tropsch synthesis (FTS) is a set of chemical reactions that use to convert a mixture of carbon monoxide and hydrogen into liquid hydrocarbons. This process is a key component of part of gas-to-liquids (GTL) technology which it is produces synthetic liquid hydrocarbons from natural gas. The FTS process has received intermittent attention as a source of low-sulfur diesel fuel and be address as the supply or cost of petroleum-derived hydrocarbons.

The most important reactions are:

i. Steam reforming $CH_4 + H_2O \leftrightarrow CO + 3H_2$

ii. CO_2 reforming $CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$

iii. Partial oxidation $CH_4 + ½\ O_2 \leftrightarrow CO + 2H_2$

iv. Water gas shift reaction $CO + H_2O \leftrightarrow CO_2 + H_2$

The production of clean fuels and synthetic diesel released by the FTS process has inspired renewed interest in both industrial and academic field recently. The super clean diesel oil fraction produced through the FTS is mainly composed by linear paraffins have high cetane numbers (more than 70) and free of sulfur and aromatics pollutants. From those derived crude oil that was the quality of this diesel offers significant environmental and efficiency benefits.

1.2 Problem Statement

Due to lack of fossil fuel, Fischer-Tropsch synthesis has become most important as synthesis gas can be produced from a large variety of sources such as natural gas, biomass, coal, etc. and the process can orienting towards a variety of products such as fuels, paraffins, alcohols, etc. Many types of cobalt supporter based catalysts in CO hydrogenation have been shown to depend on several factors such as particle size, nature of the support, the presence of promoters and pre-treatment conditions. Modification of preparation parameters is known to strongly affect the microstructure of cobalt supported catalysts. Because many disadvantage of others supporters, that's why this research just come out with this chosen, SBA-15 supporter as the best cobalt supporter in this research.

SBA-15 have been chosen because of low price cost and it's have advantages of high thermal & thermal stability. Limitations for other supporters like TiO_2 and Cab-O-Sil are lower stability and it just have short prolong life than SBA-15 in the FTS.

Additional to that, Zn and Co was chosen as precursors because it will enhance the reducibility, dispersion and influencing the stability of the cobalt catalyst in order to achieve highly stable and highly active cobalt for Fischer-Tropsch catalyst was released from E. L. Viljoen et al (2009).

1.3 Research Objectives

1. To synthesis ZnCo catalyst with different supports such as TiO_2, SBA-15 and Commercialize Cab-O-Sil.
2. To identify the characteristic of ZnCo catalyst with different supports.

1.4 Scope of Research

This research is to investigate the effect of the mesostructured materials based on silica (TiO_2, SBA-15andCab-O-Sil) as cobalt supports for preparing ZnCo based FTS catalysts. It's had explored based on recently similar research since this material represent an efficient tool to control the sizes of supported cobalt particles. For the characterization and catalytic measurements of catalyst in this research, the apparatus

that will be used such as AAS, XRD, BET surface area, TPR, TGA, FTIR SEM and N_2 adsorption-desorption.

The silica as cobalt catalyst supporter will run with additional of Zn promoter that well known as function of an electron donor to metal that can prolong life of the catalysts and has a great effect on the catalyst. Additional of Zn promoter will be effect both of the reduction rate and the density of active cobalt catalyst sites. It also lowers the temperature of the two-step conversion of cobalt oxide to cobalt metal observed in temperature programmed reduction.

The limitation of cobalt supporter will present the uniform pore size distribution in the ordered mesoporous materials that allow a better control on the cobalt crystallite size and catalytic properties and the narrow pore size distribution of the support also could prevent the sintering effect of the cobalt particles will be recorded and analyzed to compare with different cobalt supporter the level of reactivity of reaction in FTS.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

The development of new silica use as a cobalt supporter to produce a clean and good fuel in the industry has been improved time by time. This is because the cost of silica use for now was too expensive and they need to spend on it to get the best product of fuel. Due to the fumble economic problem, the new cobalt supporter has been developed from various type of silica in order to enhance the Fischer-Tropsch synthesis performance as well as low energy use and lower capital cost. In this research study, the new type of silica been focused in order to develop a new commercialize silica that can replaced the old silica that use in the industry nowadays.

Figure below showed the flow process of Fischer-Tropsch synthesis. Fischer-Tropsch synthesis is a set of chemical reactions changes a mixture of carbon monoxide and hydrogen into liquid hydrocarbons which a master key component of gas to liquids technology produces a petroleum substitute from coal, natural gas, or biomass that uses as synthetic lubrication oil and synthetic fuel.

The precursor will be used are Zn and Co. Among several example of transition metals usually use in the Fischer-Tropsch synthesis such as Co, Fe and Ru, these three types of metals which it's present the highest activity. However, Co is considered the most favourable metal for the synthesis of long-chain hydrocarbons from synthesis gas due to its high activity per weight of metal compared to Fe, high selectivity to linear paraffins, high stability toward deactivation by water which it's a by-product of the FTS process, low water–gas shift activity and low price compared to noble metals such as Ru, Re, or Pt was released by O. González et al (2009).

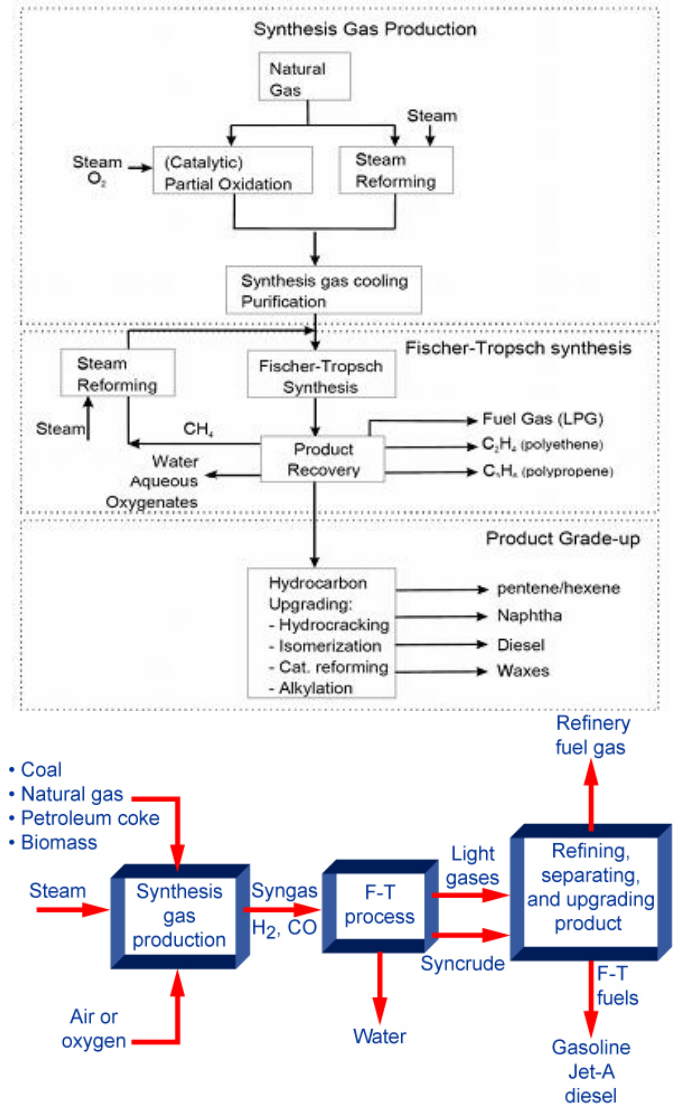

Figure 2.1 showed the Fischer-Tropsch synthesis.

2.2 SBA-15 supporter

This is a most common type mesoporous of pure silica which is a form of silica and a recent development in nanotechnology.

The SBA-15 was many used in the recent research especially about Fischer-Tropsch synthesis. The recent experiment was on the Use of different mesostructured materials based on silica as cobalt supports for the Fischer–Tropsch synthesis was released by O. González et al (2009). He published about the advantages of SBA-15 uses as cobalt supporter as saying that the use of SBA-15 as cobalt catalyst support for the FTS seems to be very promising, since the Co/SBA-15 catalyst with a Dp of 5 nm

has shown the best catalytic behavior in comparison with the rest of the materials tested in reaction such as Al- MCM-41 and INT-MM1.

He also stated that larger surface-Co species anchored or encapsulated in the wide pore mesoporous supports showed a contrary tendency. As conclusion of his statement that SBA-15 gave more great effect on the catalyst compared with other silica such as MCM-41 and INT-MM1 in his recent research.

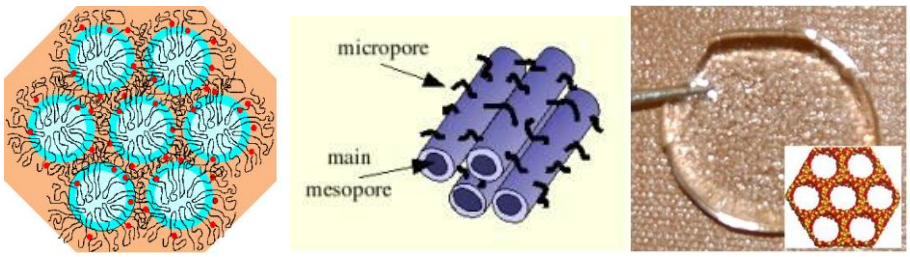

Figure 2.2 showed the structure of SBA-15.

2.3 Effects of others supporter on Co based catalysts

2.3.1 TiO_2 supporter

This is also known as titanium (IV) oxide or titania that naturally occurring oxide of titanium.

Besides of SBA-15 supporter, this research also uses for this supporter. From Antonelli et al (1999) by his thesis of Microporous Mesoporous Mater stated that the successful synthesis of stable mesoporous TiO_2 involves the application of tetra decyl phosphate surfactant as a template and removing it by calcinations.

The preparation of mesoporous TiO_2 uses dodecyl amine as the directing agent. While this solved the problem of residual phosphorous, the porous structure remained unstable after calcinations. Conclusion from his thesis was the silica of TiO_2 is the one of most stable mesoporous silica in the FTS.

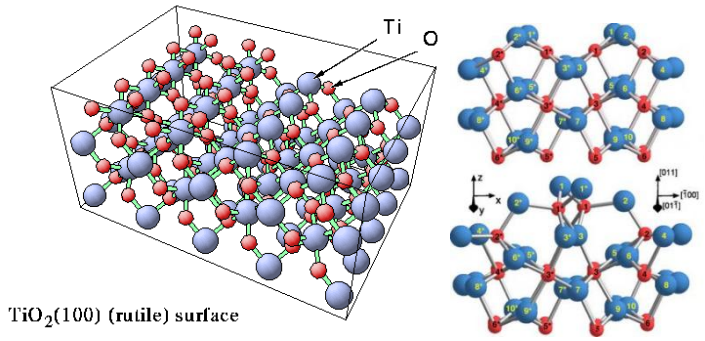

Figure 2.3 showed the structure of TiO_2.

2.3.2 Cab-o-Sil supporter

This is also known as fumed silica which consists of microscopic droplets of amorphous silica fused into branched, chainlike, three-dimensional secondary particles which then agglomerate into tertiary particles.

Cab-o-sil is still new supporter operating with Fischer-Tropsch synthesis. However, there already a lot of recent research that produce various type of cab-o-sil which it was commercial for domestic and industry uses. Amama et al (2005) stated that catalysts synthesized from Cab-O-Sil were more stable and maintained their high mesoporous structural integrity after the reaction better than those synthesized from HiSil.

Amama et al also stated that the N_2 adsorption-desorption isotherm of the former still showed a distinct capillary condensation step at p/po of 3.5 while the latter showed an inconspicuous step. As the result of these thesis statements, Cab-O-Sil was more stable than HiSil and gives more effect to catalyst reactivity in the Fischer-Tropsch synthesis.

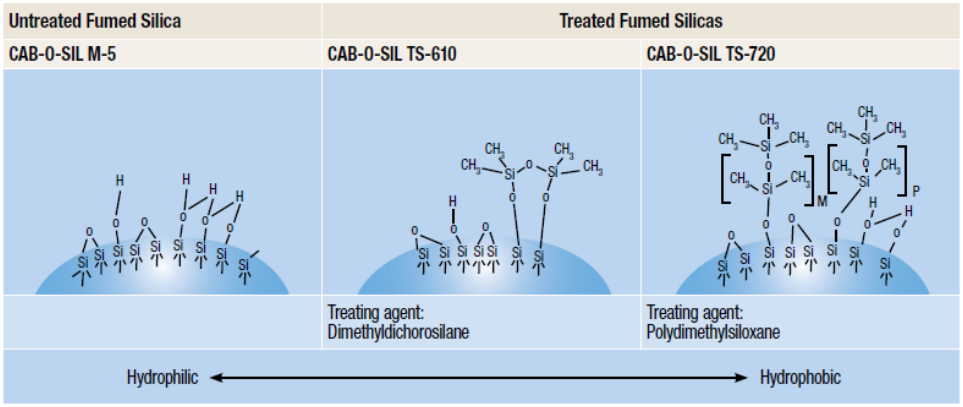

Figure 2.4 showed the structure of Cab-O-Sil.

2.4 Characterization of catalyst

2.4.1 BET

a) SBA-15

The chemical analysis results are presented in Table 2.1. Nominal and real cobalt contents were too similar. Cobalt introduction on supports based on silica leads to a sharp decrease in S_{BET} in all cases. The S_{BET} in all periodic mesoporous silicas (Al-MCM-41, SBA-15, and INT-MM1) was higher than 730 m_2/g, whereas the S_{BET} of the commercial amorphous silica was much lower (280 m_2/g).

Table 2.1: Chemical and physical properties of supports based on silica and Co-supported catalysts calcined at 350°C, (O. Gonza´ lez a, 2009).

Samples	Co content (wt.%)	Textural properties[a]						Structural properties			
		D_p[b] (nm)		V_p (cm^3/g)		S_{BET}[b] (m^2/g)		Co dispersion (%)	Co^0 crystallite size (nm)	Reduced Co fraction (%)	Co_3O_4[c] average crystallite size (nm)
SBA-15	-	4.9		0.87		781		-	-	-	-
Al-MCM-41 (Si/Al) = 100	-	3.2		0.93		860		-	-	-	-
INT-MM1	-	2.6		0.66		730		-	-	-	-
SiO_2 amorphous	-	8.4		0.79		280		-	-	-	-
		Fresh[d]	Used[e]	Fresh[d]	Used[e]	Fresh[d]	Used[e]				
Co/SBA-15	18.1	4.8	5.1	0.62	0.20	538	205	3.0	32.6	81	14.6
Co/Al-MCM-41	17.7	3.2	3.4	0.66	0.23	625	212	5.3	18.1	44	7.0
Co/INT-MM1	20.9	3.1	3.6	0.50	0.15	584	170	4.7	20.3	36	6.8
Co/SiO_2	19.3	8.1	8.3	0.54	0.36	209	136	2.1	45.8	94	14.9

[a] Values obtained from N_2 adsorption-desorption isotherms.
[b] D_p and surface area values obtained by means of the BJH and BET methods, respectively.
[c] Values calculated using the Scherrer equation for the more intense peak ($2\theta = 36.8^\circ$).
[d] Calcined samples.
[e] Used samples in FTS for 70 h on stream.

Compared to the pure mesoporous silicas, a reduction of S_{BET} and V_p is noted for all catalysts after incorporation of ~20 wt. % Co. The decrease may be attributed to the dilution effect of the support caused by the presence of the supported cobalt oxide phase or to a partial blockage of the support pores especially micropores and mesopores occurred after Co incorporation. Textural properties comparison between the fresh and used catalysts has been performed in order to evaluate their hydrothermal stability.

Other observations suggested that the ordered structures of these mesoporous materials under reaction conditions continue collapsing in varying degree depending on their hydrothermal stability and depending on the pore wall thickness of mesoporous material. Thus, according to the differences between Dp, S_{BET} and Vp noticed for fresh and used catalysts might be established a hydrothermal stability order for all mesoporous materials as follows: Co/SBA-15 > Co/Al-MCM-41 > Co/INT-MM1.These observed variations in Dp, S_{BET} and Vp attributed to the accumulation of the waxes deposited in the catalyst pores.

b) TiO_2

From Table 2.2 below shows the textural properties of the silica supports and the titania loaded samples: S_{BET}, specific surface area; V_P, pore volume, and pore size corresponding to the maxima of the plotted pore size distributions. The TiO_2 supports within a range of 2 to 25 nm of pore size tested in order to get the influence of the silica pore size in the growth of the titania particles. The mesoporous ordered material MCM-41, which presented the higher BET surface area which it's had a mean pore size of 2.3 nm.

Table 2.2: Textural properties of supports and prepares samples, (Rosenthal et al, 2008).

	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Maximum of the pore size distribution (nm)
MCM-41 SiO_2	1051	0.83	2.3
SBA-15 SiO_2	640	0.96	7.5
SBA-15/TMB SiO_2	601	1.62	20.0
Commercial SiO_2	317	1.59	27.5
100% TiO_2 Reference	9	-	-
20% TiO_2 MCM-41	294	0.57	16.0
20% TiO_2 SBA-15	532	0.78	7.0
40% TiO_2 SBA-15	442	0.69	6.5
60% TiO_2 SBA-15	349	0.60	6.5
20% TiO_2 SBA-15/TMB	517	1.40	18.5
40% TiO_2 SBA-15/TMB	414	1.08	18.5
60% TiO_2 SBA-15/TMB	304	0.78	18.5
20% TiO_2 Commercial	299	1.16	22.5
40% TiO_2 Commercial	246	0.94	25.0
60% TiO_2 Commercial	179	0.67	26.0

The average pore size of 7.5 nm of the hexagonal mesoporous silica structure SBA-15 was modified by the addition of trimethyl benzene in the synthesis as it has been explained above. The resulting material that SBA-15/TMB presents the pore size value of 20.0 nm whereas the BET surface area was slightly lower than the presented by the unmodified SBA-15 silica. Finally, it can be observed that the non-structured commercial silica offered the highest pore size value (27.5 nm) and the smaller surface BET area.

c) Cab-o-sil

From Table 2.3 below, the physical properties of the catalysts used in this study presented in figure above. The results of data above as shown in figure above revealed that Cab-o-Sil had larger pore diameter and pore wall thickness but had smaller S_{BET} and pore volume compared to HiSil. So that the reactivity of silica supporter will limited by these criteria in order to get into the maximum level. However, Cab-o-sil had just small different of all the textures properties and just got difference in range of 0.08-2.50 in pore diameter, 0.36-0.442 in volume, 175-578 in S_{BET} and 0.56-1.83 in pore wall thickness .

Table 2.3: Textural Properties of the Various Catalysts Synthesized from Hisil and Cab-O-sil, (Amama et al, 2005).

colloidal silica	Fe content in synthesis gel (wt %)	Fe content in sample by ICP (wt %)	pore diameter (Å)	pore volume (cc/g)	S_{BET} (m^2/g)	d_{100} (Å)	pore wall thickness (Å)	color of calcined sample
HiSil	0		26.89	1.069	1218	35.50	14.10	white
HiSil	1.0	0.99	28.77	0.94	1073	38.50	15.68	white
HiSil	2.0	1.59	29.30	1.01	1144	39.92	16.79	pale yellow
HiSil-R[a]	2.0		25.08	0.24	304			black
HiSil-O[b]	2.0		26.23	1.167	1089			pale yellow
HiSil	3.0	2.25	28.60	0.44	514			brown
Cab-O-Sil	0		27.33	0.935	1045	38.29	16.88	white
Cab-O-Sil	1.0	0.99	29.52	0.813	898	39.61	16.24	white
Cab-O-Sil	2.0	1.78	29.38	0.87	969	41.58	18.63	pale yellow
Cab-O-Sil-R[a]	2.0		27.58	0.682	882			black
Cab-O-Sil-O[b]	2.0		26.84	0.926	990			pale yellow
Cab-O-Sil	3.0	2.37	29.37	0.80	909	42.05	19.19	brown

[a] After reaction. [b] After carbon removal (TPO).

2.4.2 N_2 adsorption–desorption isotherms

a) SBA-15

From Figure 2.5, the shapes of these isotherms are typical for mesostructured materials and occur on porous adsorbents possessing pores in the diameter range from 2 to50 nm. The isotherms for the SBA-15 presented a sharp inflection in the range of relative pressure from 0.7 to 0.8 indicative of good-quality SBA-15 material with uniform mesopores. This reveals a wide pore size distribution that corresponds to a macroporous material.

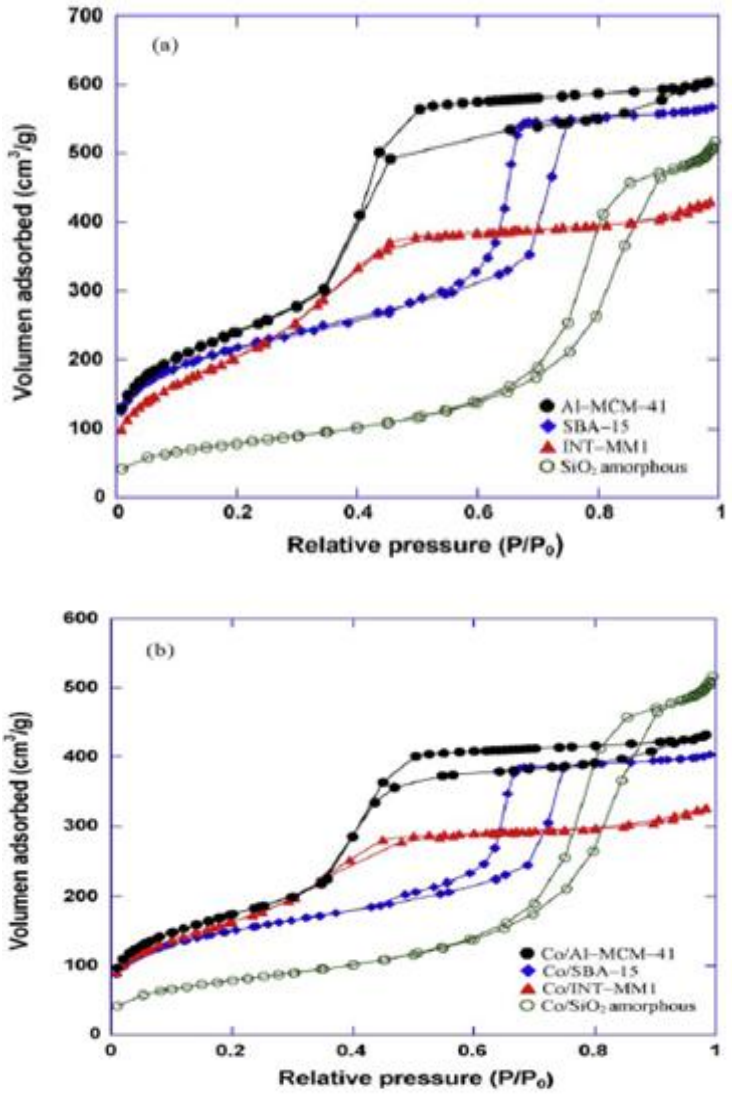

Figure 2.5: Nitrogen adsorption–desorption isotherms obtained at 196°C, (a) Supports based on silica and (b) Co catalysts supported on silica supports, (O. Gonza´ lez a, 2009).

For the Al-MCM-41, the sharp increase observed in adsorbed volume at 0.3–0.4 relative pressure. The previous results obtained from the density function theory (DFT) method for the INT-MM1gave a Dp of 2.5 nm and a bimodal pore distribution, with approximately 55% mesoporosity and 45% microporosity contributing to the total surface area of this material. The bimodal pore supports such as SBA-15 and INT-MM1 contain large and small pores simultaneously. The small pores could yield the sites for anchoring smaller cobalt oxide particles, while the large pores could provide a network for fast diffusion of reacting molecules and products.

The shapes of the N_2 adsorption isotherms of Co supported samples are similar to their corresponding siliceous supports which it's suggesting that the mesoporous structure was mostly retained upon Co impregnation in all cases. This observation is in agreement with previous reports in the recent researches.

b) TiO_2

From Figure 2.6, the isotherms of the SBA-15 based samples kept the features of the isotherm exhibited by the unloaded support. Therefore, it is concluded that the mesostructure is maintained upon TiO_2 addition. Moreover, it is interesting to note that the calculated pore size distribution (Figure above c) is slightly modified even for the sample with the highest titania loading, suggesting a porous structure similar to that present in the unloaded support.

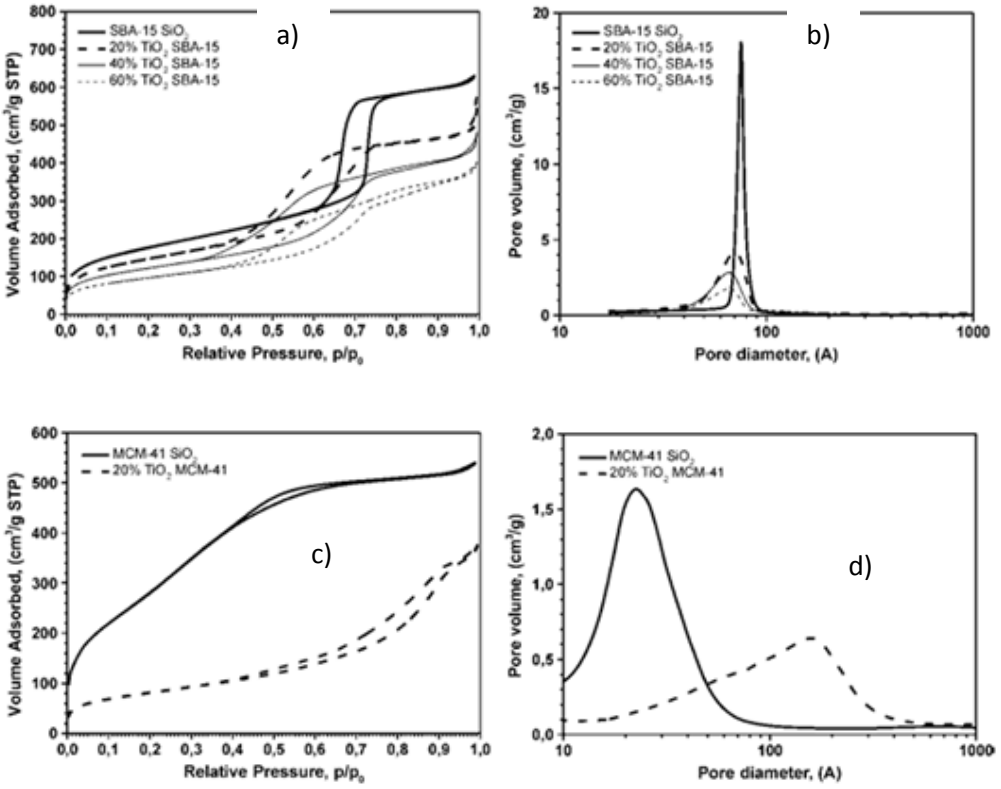

Figure 2.6: (i) Nitrogen adsorption isotherms of: a) 0 – 60 % TiO_2& SBA-15 and b) 0 – 20% TiO_2& MCM-41 samples. (ii) Pore size distributions of: c) 0 – 60 % TiO_2& SBA-15 and d) 0 – 20% TiO_2& MCM-41 samples, (Zhang et al, 2005).

Similar results were obtained in the case of the SBA-15/TMB based samples. On the other hands, it can be observed in the 20%TiO_2&MCM-41 sample how the titania loading significantly changes the isotherm shape of the support, which is indicative of structure modifications. In addition, the shift of the pore size distribution maximum too much higher values and the wider pore size distribution (Figure 2.6 d) indicates the breakdown of the structured pore arrangement.

c) Cab-o-sil

From Figure 2.7, the isotherm corresponding to p/po< 0.3 represents the monolayer adsorption of N_2 on the walls of the mesopore, while that with p/po> 0.4 represents the multilayer adsorption on the outer surface of the particles. The point at which the inflection begins is related to the capillary condensation within the uniform mesopores and their diameter. There was a slight shift in the inflection step toward higher p/po upon the introduction of Fe.

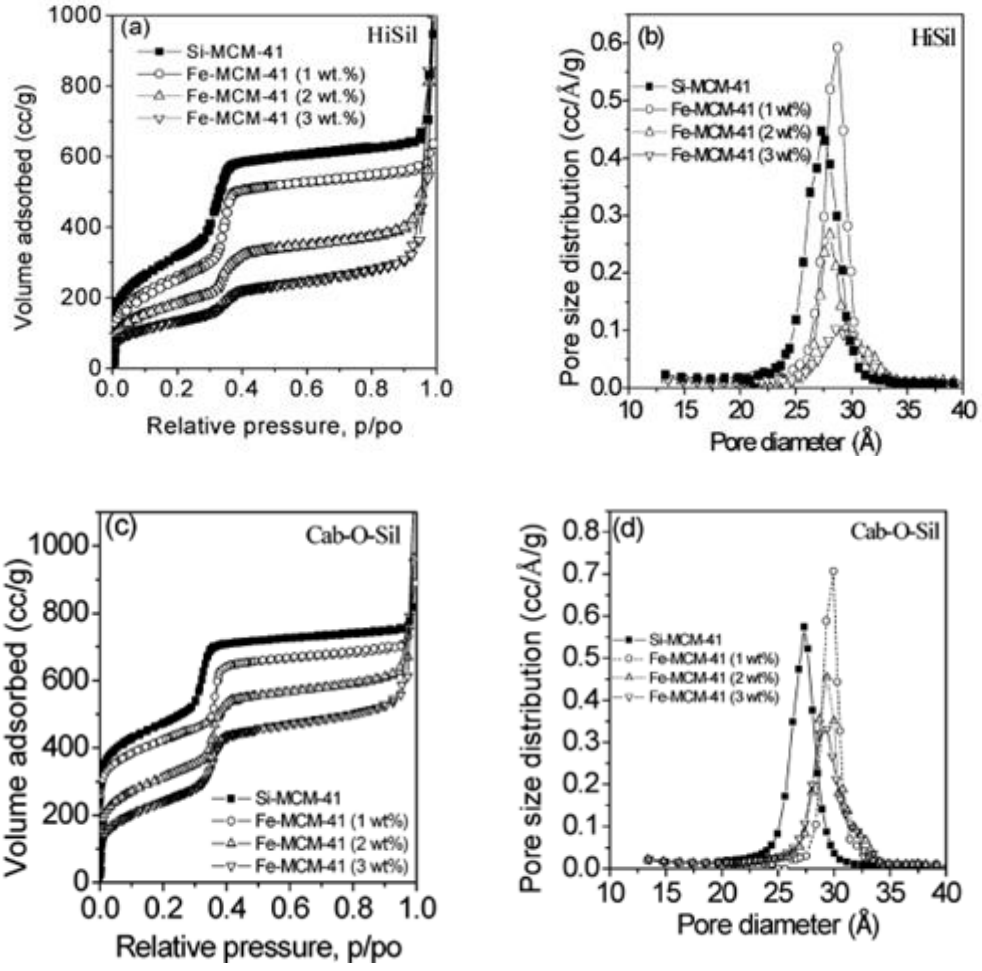

Figure 2.7: N_2 adsorption-desorption isotherms of Si-MCM-41 and Fe-MCM-41 (1, 2, and 3 wt %) and their respective pore size distributions synthesized from HiSil (a) and (b) and Cab-O-Sil (c) and (d), (Amama et al, 2005).

This signifies an increase in pore size, in consonance with XRD results. There was no noticeable shift in the inflection step ofFe-MCM-41 upon incorporation of more Fe^{3+}cations. The value of the slope increased upon the initial introduction of Fe (1 wt %) into the silica framework because of the knitting effect in consonance with previous observation. Further increase in the amount of Fe (>1 wt %) resulted in a decrease in the value of slope, which could be attributed to the oversaturation of Fe^{3+} in the pore walls of MCM-41. The effect of Fe loading on the full width at half-maximum (fwhm) of the pore size distribution (PSD) curve is shown in figure above. There is a general decrease in the fwhm of the PSD curve upon the incorporation of 1 wt% of Fe. However, as the Fe amount in MCM-41 is increased beyond 1 wt %, the fwhm increases suggesting a decrease in the structural order. The behaviors of the fwhm of the PSD curves and of the slopes of the capillary condensation steps upon incorporation of different concentrations of Fe into MCM-41were in consonance.

Therefore, its conclude as follows: (i) there is a significant structural improvement upon the incorporation of 1 wt % of Fe into MCM-41, but a decrease in the structural integrity is observed upon incorporation of higher Fe concentrations, (ii) siliceous MCM-41 and Fe-MCM-41 synthesized from Cab-O-Sil have higher structural order in comparison to those synthesized from HiSil, as evidenced by their higher values for capillary condensation slopes and lower fwhm of the PSD curves. It can just be assumed that the type and the amount of impurities present in these colloidal silica and their synthesis routes may rationalize this observation.

2.4.3 XRD

a) SBA-15

From Figure 2.8, the XRD patterns for all cobalt catalysts supported on mesoporous silicas are presented in figure above. These show five sharp signals characteristic of Co_3O_4 spinel (PDFWIN 42-1467) and one broad signal with low intensity located at $2\Theta = 238$ typical of siliceous materials. The latter signal is attributed

to diffuse dispersion caused by the lack of long-range order of Si atoms located on the walls of the channels in the materials based on silica. The XRD peaks become narrower and more intense for the Co/SiO_2 and Co/SBA-15 catalysts, indicating the presence of larger and easier to reduce Co_3O_4 crystallite size in these materials in comparison with the Co/Al-MCM-41 and Co/INT-MM1 solids.

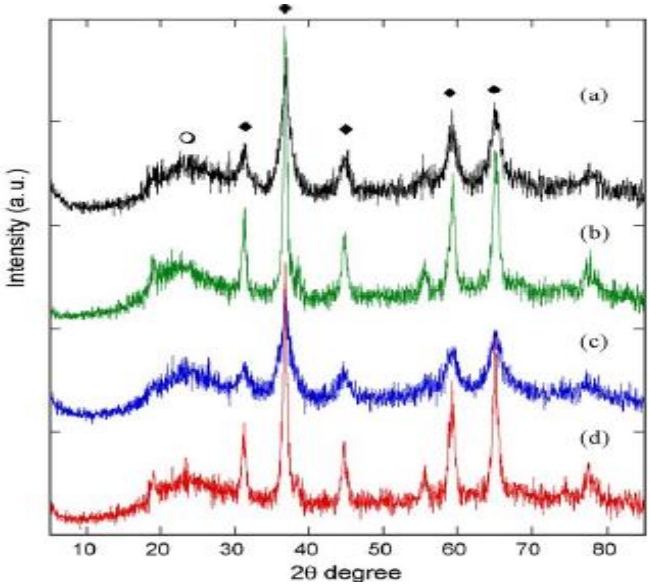

Figure 2.8: XRD patterns of cobalt-supported catalysts, (a) Co/Al-MCM-41, (b) Co/SiO_2 amorphous, (c) Co/INT-MM1, and (d)Co/SBA-15. Identified phases: (○) amorphous SiO2 and (●) Co_3O_4 spinel, (O. Gonza´ lez a, 2009).

This observation can be correlated with the Co_3O_4 average crystallite size data and supported the results of reduced Co fraction presented in previous Table 2.1, where is clearly showed that the Co/SiO_2 and Co/SBA-15 samples exhibit the largest Co_3O_4 average crystallite size (~15 nm) and the higher reduced Co fraction (>80%). In this sense, strong metal-support interactions and consequently higher Co dispersion percentages are expected to be found in the Co/Al-MCM-41 and Co/INT-MM1 catalysts. On the one hand, Table 2.1 shows that the sizes of the supported Co_3O_4 crystallites depend on silica porous structure, specifically from Dp since larger Co_3O_4 crystallite sizes are found in the catalysts prepared from the support with wider pores (SBA-15 and commercial SiO_2) and vice versa (Al-MCM-41 and INT-MM1). On the other hand, Table 2.1 also shows in all cases that the Co_3O_4 crystallite size values estimated for the catalysts exceed the Dp values calculated for their corresponding supports.